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COATING and CHEMICAL LABORATORY

AS AD No. 249 437

AMINO-CARBOXYLIC AMPHOTERIC SURFACTANTS IN ALKALINE CLEANERS

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D. A. Project No. 593-32 006

Author A. Mankowich

Date 9 November 1960

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MARYLAND

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AMINO-CARBOXYLIC AMPHOTERIC SURFACTANTS IN ALKALINE CLEANERS

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Dept of the Army Project No. 593-32-006

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ABSTRACT

A study was made of amino-carboxylic amphoteric surfactants in soak-type alkaline cleaners suitable for use with aluminum and magnesium (nonferrous) alloys as well as with ferrous materials. Compounds were developed possessing the "improved detergency" necessary for the removal of asphalt and mineral oil soils. The surfactant portion of such compounds may consist of as little as 1.0 percent of the partial sodium salt of N-lauryl beta iminodipropionate plus 1.0 percent of a polyethanoxy nonyl phenol (15-30 ethylene oxide mole ratio). Galvanic corrosion tests using magnesium-aluminum couples indicated satisfactory behavior of the aluminum, the anodic member of the couple, as well as of the magnesium.

The developed cleaners meet all the performance requirements of Fed. Spec. P-C-436a (Cleaning Compound, Alkali Type) except surface tension.

I. INTRODUCTION

Previous studies by this Laboratory of the detergent characteristics of amphoteric surfactants in alkaline cleaners have included investigations of agents of the quaternary imidazolium hydroxide type (1,2). It was found that the undecyl or coconut oil derivative of such surfactants combined with specific anionic or nonionic syndets and alkaline salts produced granular, free-flowing formulations complying with the cleaning and surface tension requirements of Federal Specification P-C-436a, covering a soak type alkaline cleaner suitable for use with both ferrous and nonferrous materials. In meeting the detergency requirements of P-C 436a, cleaners containing the quaternary imidazolium hydroxide amphoterics indicated they were of "improved detergency", which we have defined as possession by the cleaner of high hydrophile plus moderate lipophile strength as evidenced by the ability to remove asphalt and mineral oil soils respectively. It was also discovered that one of the amphoterics, the dicarboxylic analogue of the coconut oil derivative, was particularly effective. Compounds containing only 3 percent of the latter plus 1.5 percent of octylphenyl nonaethylene glycol ether possessed excellent detersive, heat stability and cleaning capacity characteristics.

In this investigation, amino-carboxylic amphoterics have been studied in soak type alkaline cleaners. These agents are N-substituted amino acid condensates of fatty primary amines and acrylic monomers. Their structure is illustrated by the following formula:

$$H_{25}C_{12}\text{-}\underset{\underset{H}{|}}{N}\text{-}CH_2\text{-}CH_2\text{-}COONa$$

The above agent is sodium N-lauryl beta aminopropionate. In alkaline solution, the negatively-charged carboxylic group predominates, and the amphoteric acts anionically.

II. DETAILS OF TEST

A. Test Methods

The test methods used in this investigation were those given in Federal Specification P-C-436a, "Cleaning Compound, Alkali Type". Materials complying with this specification are capable of 100 percent asphalt removal in not more than 21 minutes in the standardized cleaning test. In the studies reported herein, the asphalt cleaning time was 21 minutes unless completeness of soil removal was observed prior to that time.

1. Surfactants

The amphoteric surfactants used in this investigation were flaked materials, with a 96 percent minimum active content. They consisted of the following:

#1 - sodium N-coco beta-aminopropionate
#2 - disodium N tallow beta-iminodipropionate
#3 - partial sodium salt of N-lauryl beta-iminodipropionate

B. Results

1. Cleaners with Amphoteric No. 1 - Table I

A cleaner containing amphoteric No. 1 as a substitute for the alkyl aryl sulphonate - polyethanoxyalkyl phenol combination of the Standard Comparison Compound of Fed. Spec. P-C-436a failed to remove mineral oil from the steel test panels. As little as a 1.0 percent addition of a polyethanoxy-alkyl phenol to a dry cleaner also containing amphoteric No. 1 imparted mineral oil detergency to the cleaner solution.

Excellent asphalt and mineral oil detergency was obtained from compounds containing 9.0-1.5% amphoteric No. 1 combined with 9.0-5.0% isooctylphenyl-nonaethylene glycol ether (IOPNG). A surfactant combination of 1.0% amphoteric No. 1 plus 5.0% IOPNG gave poor asphalt detergency.

When nonylphenylpentadecaethylene glycol ether (NPPGE) replaced IOPNG as the nonionic additive, excellent asphalt and mineral oil detergency could be obtained from cleaners with 1.0% amphoteric No. 1 plus 2.0% NPPGE; reduction of the NPPGE content to 1.0% resulted in poor asphalt detergency. Results with nonylphenyltricontaethylene glycol ether (NPTGE) as the nonionic additive duplicated of those with NPPGE.

2. Cleaners with Amphoteric No. 2 - Table II

Cleaners containing 1.0% amphoteric No. 2 and 1.0% NPPGE or NPTGE possessed poor mineral oil detergency as well as poor asphalt detergency. Increasing the NPPGE content to 2.0% resulted in good asphalt and mineral oil cleaning; but an increase to 2.0% NPTGE still gave poor asphalt removing properties.

3. Cleaners with Amphoteric No. 3 - Table III

Cleaners with 1.0% amphoteric No. 3 plus 1.0% of either NPPGE, NPTGE or nonylphenyleicosaethylene glycol ether (NPEGE) possessed good asphalt and mineral oil detergency. In order to obtain good asphalt detergency from cleaners containing 1.0% amphoteric No. 3 and sodium dodecyl benzene sulphonate (98.+% active), SDBS, the latter content could not be dropped below 5.0%.

A cleaner containing 1.0% amphoteric No. 3 plus 1.0% NPTGE passed the stability requirement of Fed. Spec. P-C-436a. This composition made up with 86 PPM hard water passed the cleaning requirements of P-C-436a.

4. Galvanic corrosion tests - Table IV

Table IV contains the data and results of galvanic corrosion tests using AZ31 magnesium alloy and 2S aluminum in the area ratio of 2:1 with developed cleaning solutions containing amphoteric No. 3. The area

ratio was selected to accentuate the corrosion of the aluminum, which is the anodic member of the couple in alkaline solution. In Solution No. 1 (7.5% solution), the silicate content is high enough to inhibit completely the solution of aluminum which actually gains several tenths of a milligram and remains bright. In Solution No. 2 (a 0.5% solution), there is less silicate available for inhibition, and the aluminum loses 0.7 - 0.8 mg in 2 hours boiling, but remains bright and shiny. This degree of loss is not considered "corrosive" to 2S aluminum (Fed. Spec. P-S-731, Steam Cleaning Compound, permits 1.2 mg. loss in 1 hours boiling for 2S aluminum with twice the area). The magnesium members of the couples darken slightly, but their small gains in weight indicate negligible corrosive effect. They can be brightened by dipping in 5% HNO_3 for a few seconds, followed by water rinsing.

5. Discussion

Examination of the data in Tables I, II and III indicates that amphoteric No. 3, the partial sodium salt of N-lauryl beta-iminodipropionate, is the most effective detergent of the animo-carboxylic surfactants studied herein. It is the only one of the latter type which, when present to the amount of 1.0% in a cleaner, requires only 1.0% of added polyethanoxy nonyl phenol to impart "improved detergency" (ability to remove asphalt and mineral oil soils) to that cleaner. Amphoterics No. 1 and No. 2 rate behind amphoteric No. 3, in that order. However, any of these three amino-carboxylic surfactants in combination with a polyethanoxy nonyl phenol forms a very powerful detergency combination, with at most only 1.0% of the former plus 2.0% of the latter required for maximum detergent effects in a medium pH cleaner (ca 12.1 pH at 25°C in 7.5% solution).

The marked superiority of the polyethanoxy nonyl phenols (15 and 30 mols ethylene oxide) over the polyethanoxy octyl phenol (9 mols ethylene oxide) is to be noted in the tests with amphoteric No. 1. It would seem that, since asphalt detergency requires higher hydrophile strength, and since the aforementioned nonylphenols possess higher HLB numbers than the octylphenol, the reason for the superiority is simply a matter of the greater hydrophilicity of the nonyl phenols.

It should be noted, also, that the surface tension values of the cleaning solutions containing the amino-carboxylic amphoterics and polyethanoxy nonyl phenols are considerably higher than the requirement of Fed. Spec. P-C-436a. For example, 0.05% solutions of cleaners containing (1.0% amphoteric No. 3 plus 1.0% NPPGE) and (1.0% amphoteric No. 3 plus 1.0% NPTGE) had surface tensions of 49.1 and 53.0 dynes per cm, respectively (P-C-436a maximum is 36 dynes/cm). Amphoteric No. 3, especially, possesses poor surface tension depressant properties, and the polyethanoxy nonyl phenols also are poor depressants. These facts, combined with the low surfactant concentrations prevailing in the specification test, are responsible for the high values given above.

III. REFERENCES

1. Mankowich, A., "Coating & Chemical Laboratory Report No. 34, October 1957.
2. Mankowich, A., Coating & Chemical Laboratory Report No. 62, August 1958.

APPENDIX

Tables

Table I

No. 1 - Amphoteric Cleaners

Cleaner Composition - % By Weight					Asphalt Detergency	Mineral Oil Detergency
$Na_2SiO_3 \cdot 5H_2O$	$NaH_2PO_4 \cdot H_2O$	$Na_3PO_4 \cdot 12H_2O$	Amphoteric	Additive		
34.5	12.0	33.5	20.0	None		3 tests-all fail
36.7	12.8	35.5	9.0	6.0*	9 Min; 21 Min.	2 tests-pass
36.7	12.8	35.5	6.0	9.0*	15 Min; 15 Min	2 tests-pass
38.0	13.2	36.8	6.0	5.0*	12 Min; 12 Min	2 tests-pass
39.7	13.8	38.5	3.0	5.0*	18 Min; 18 Min	2 tests-pass
40.4	14.0	39.1	1.5	5.0*	21 Min; 21 Min	2 tests-pass
40.6	14.1	39.3	1.0	5.0*	poor: 1.5-24.0 mg. left	2 tests-pass
40.4	14.0	39.1	1.5	5.0**	15 Min; 15 Min	2 tests-pass
40.6	14.1	39.3	1.0	5.0**	18 Min; 18 Min	
41.1	14.2	39.7	1.0	4.0**	18 Min; 15 Min	2 tests-pass
41.5	14.4	40.1	1.0	3.0**	21 Min; 18 Min	2 tests-pass
41.9	14.6	40.5	1.0	2.0**	21 Min; 21 Min	2 tests-pass
42.3	14.8	40.9	1.0	1.0**	poor: 0.5-14 mg. residue	2 tests-pass
41.9	14.6	40.5	1.0	2.0***	15 Min; 18 Min	2 tests-pass
42.3	14.8	40.9	1.0	1.0***	poor: 34-35 mg residue	2 tests-pass

NOTES: All solution concentrations are 7.5% (grams compound per 100 ml solution)
Asphalt Detergerncy of Standard Comparison Compound of P-C-436a= 21 Minutes
Additives:
* - isooctylphenylnonaethylene glycol ether (IOPNG)
** - nonylphenylpentadecaethylene glycol ether (NPPGE)
*** - nonylphenyltricontaethylene glycol ether (NPTGE)

Table II

No. 2 Amphoteric Cleaners

Cleaner Composition - % By Weight					Asphalt Detergency	Mineral Oil Detergency
$Na_2SiO_3 \cdot 5H_2O$	$NaH_2PO_4 \cdot H_2O$	$Na_3PO_4 \cdot 12H_2O$	Amphoteric	Additive		
42.3	14.8	40.9	1.0	1.0**	poor: 29.-95 mg. residue	2 tests-fail
41.9	14.6	40.5	1.0	2.0**	21 Min; 21 Min	2 tests-pass
41.5	14.4	40.1	1.0	3.0**	21 Min; 21 Min	2 tests-pass
40.6	14.1	39.3	1.0	5.0**	18 Min; 15 Min	2 tests-pass
40.4	14.0	39.1	1.5	5.0**	21 Min; 18 Min	2 tests-pass
42.3	14.8	40.9	1.0	1.0***	poor: 43 mg. residue	1 test of 2-fails
41.9	14.6	40.5	1.0	2.0***	poor: 47-59 mg. residue	2 tests-pass

NOTE: Additives - See Table I

Table III

No. 3 Amphoteric Cleaners

Cleaner Composition - % By Weight					Asphalt Detergency	Mineral Oil Detergency
$Na_2SiO_3 \cdot 5H_2O$	$NaH_2PO_4 \cdot H_2O$	$Na_3PO_4 \cdot 12H_2O$	Amphoteric	Additive		
42.3	14.8	40.9	1.0	1.0**	border-line: 0.1-0.4 mg. residue	2 tests-pass
42.3	14.8	40.9	1.0	1.0***	15 Min; 16 Min	2 tests-pass
42.3	14.8	40.9	1.0	1.0 ▽	20 Min; 21 Min	2 tests-pass
40.6	14.1	39.3	1.0	5.0 □	18 Min; 15 Min	2 tests-pass
41.3	14.2	40.0	1.0	3.5 □	poor: 27 mg residue	
41.9	14.6	40.5	1.0	2.0 □	poor: 55 mg. residue	
42.3	14.8 (see note)	40.9	1.0	1.0***	border-line: 2 mg. residue	2 tests pass

NOTES: Additives - Table I and following:
▽ - nonylphenyl eicosaethylene glycol ether (NPEGE)
□ - sodium dodecyl benzene sulphonate (SDBS)
Last cleaner in Table: boiled 40 hours prior to cleaning tests (Stability Test of Fed. Spec. P-C-436a)
Cleaner with (1.0% Amphoteric No. 3 plus 1.0% NPTGE) passed mineral oil and asphalt cleaning tests in 86PPM hard water.

Table IV

Galvanic Corrosion Tests

Material:

Magnesium Alloy (AZ31), Fed. Spec. QQ-M-44, 3 inches x 3/4 inch x .030 inch approx.
Aluminum Alloy 1100 (2S), Fed. Spec. QQ-A-561, 1½" x 3/4" x .030 " approx.
Panels fastened by cotton string thru two 1/16 inch holes, one near each short end of aluminum panel.

Solution No. 1:

Test consisted of 2 hours boiling in 200 ml. of following:

7.5% solution (7.5 grams compound per 100 ml solution) of cleaner containing Amphoteric No. 3, as below:

Solution No. 2:

Test consisted of 2 hours boiling in 200 ml. of following:

0.5% solution (0.5 grams compound per 100 ml solution) of cleaner containing Amphoteric No. 3, as follows:

$Na_2SiO_3.5H_2O$	41.9% by weight
$NaH_2PO_4.H_2O$	14.6% by weight
$Na_3PO_4.12H_2O$	40.5% by weight
Amphoteric No. 3	1.0% by weight
NPPGE	2.0% by weight

Results:

Solution No. 1:

Magnesium - - - - gained 0.7 mg - 0.8 mg; very slightly darkened
Aluminum - - - - gained 0.3 mg - 0.2 mg; bright

Solution No. 2:

Magnesium - - - - gained 1.4 mg - 1.6 mg - 1.5 mg - 1.6 mg; darkened
Aluminum - - - lost 0.7 mg - 0.8 mg - 0.8 mg - 0.7 mg; bright

DEPARTMENT OF THE ARMY
U.S. ARMY RESEARCH, DEVELOPMENT AND ENGINEERING COMMAND
3071 ABERDEEN BOULEVARD
ABERDEEN PROVING GROUND, MARYLAND 21005-5201

REPLY TO
ATTENTION OF

05 NOV 2012

RDCB-DPC-RS

MEMORANDUM THRU Director, Edgewood Chemical Biological Center, (ECBC) (RDCB-D), 5183 Blackhawk Road, Aberdeen Proving Ground, MD 21010-5424

FOR Office of the Chief Counsel, US Army Research, Development and Engineering Command (RDECOM) (AMSRD-CCF/Ms. Kelly Knapp), 3071 Aberdeen Boulevard, Aberdeen Proving Ground, MD 21005-5424

SUBJECT: Operations Security/Freedom of Information Act (FOIA) Review Request

1. The purpose of this memorandum is to recommend the release of information in regard to RDECOM FOIA Request, FA-13-0001.

2. On 2 October 2012, the Edgewood Chemical Biological Center (ECBC) received RDECOM FOIA Tasker #FA-13-0001. The request originated from the Defense Technical Information Center (DTIC) at Fort Belvoir, VA.

3. The following documents were reviewed by Subject Matter Experts from ECBC and deemed appropriate for both downgrade and release:

a. AD 149572, Amphoteric Surfactants in Alkaline Cleaners, 30 Oct 57.

b. AD 206020, Low Surfactant Content Amphoteric Cleaners, 13 Aug 1958.

c. AD 249437, Amino Carbolic Amphoteric Surfactants in Alkaline Cleaners, 9 Nov 1960.

4. The ECBC point of contact for this action is Mr. Ronald L. Stafford, 410-436-6810 or ronald.l.stafford.civ@mail.mil.

JUNE K. SELLERS
Security Manager